

Accepted Manuscript

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PII: S0019-1035(14)00408-4

DOI: <http://dx.doi.org/10.1016/j.icarus.2014.07.023>

Reference: YICAR 11189

To appear in: *Icarus*

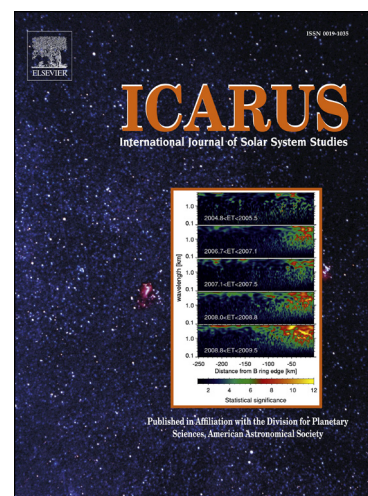
Received Date: 4 May 2014

Revised Date: 18 July 2014

Accepted Date: 18 July 2014

Please cite this article as: Boxe, C.S., Francisco, J.S., Shia, R.-L., Yung, Y.L., Nair, H., Liang, M.-C., Saiz-Lopez, A., New Insights into Martian Atmospheric Chemistry, *Icarus* (2014), doi: <http://dx.doi.org/10.1016/j.icarus.2014.07.023>

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New Insights into Martian Atmospheric Chemistry

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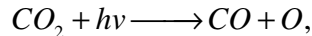
In submission to Icarus

Abstract

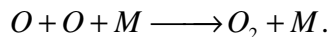
HO_x radicals are produced in the Martian atmosphere by the photolysis of water vapor and subsequently participate in catalytic cycles that recycle carbon dioxide (CO_2) from its photolysis product carbon monoxide (CO), providing a qualitative explanation for the stability of its atmosphere. Balancing CO_2 production and loss based on our current understanding of Martian gas-phase chemistry has, however, proven to be difficult. The photolysis of O_3 produces $\text{O}(^1D)$, while oxidation of CO produces HOCO radicals, a new member of the HO_x family. The $\text{O}(^1D)$ quantum yield has recently been updated, which quantifies nonzero quantum yields in the Huggins bands. In Earth's atmosphere HOCO is considered to be unimportant since it is quickly removed by abundant oxygen molecules. The smaller amount of O_2 in the Mars' atmosphere causes HOCO's lifetime to be longer in Mars' atmosphere than Earth's (3×10^{-5} seconds to 1.2 days from Mars's surface to 240 km, respectively). Limited kinetic data on reactions involving HOCO prevented consideration of its reactions directly in atmospheric models. Therefore, the impact of HOCO reactions on Martian chemistry is currently unknown. Here, we incorporate new literature rate constants for HOCO chemistry and an updated representation of the $\text{O}(^1D)$ quantum yield in the Caltech/JPL 1-D photochemical model for Mars' atmosphere. Our simulations exemplify perturbations to NO_y , HO_x , and CO_x species, ranging from 5 to 50%. The modified $\text{O}(^1D)$ quantum yield and new HOCO chemistry cause a 10% decrease and a 50% increase in OH and H_2O_2 total column abundances, respectively. At low altitudes, HOCO production contributes 5% towards CO_2 production. Given recent experimentally-obtained branching ratios for the oxidation of CO , HOCO may contribute up to 70% toward the production of NO_y , where HO_x and NO_y species are enhanced up to a factor 3, which has implications for rethinking the fundamental understanding of NO_y , HO_x , and CO/CO_2 cycling on Mars. Two new reaction mechanisms for converting CO to CO_2 using HOCO reactions are proposed, which reveal that H_2O_2 is more intimately coupled to CO_x chemistry. Our simulations are in good agreement with satellite/spacecraft measurements of CO and H_2O_2 on Mars.

I. Introduction

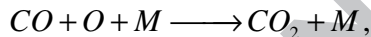
Mars continues to be a test-bed for space exploration for finding extraterrestrial life. At present, finding life on Mars may not be limited by essential life nutrients, such as water and nitrogen (Boxe et al., 2012a; Boxe et al., 2012b). It's atmosphere is comprised primarily of carbon dioxide (Owen, 1977), approximately $\sim 95\%$, which is readily photolyzed by solar ultraviolet radiation below 205 nm to produce carbon monoxide (CO) and atomic oxygen (O):



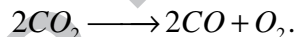
where atomic oxygen forms O_2 via the following reaction:



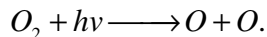
Once CO_2 is converted into CO and O, it is difficult to restore it. This is primarily due to the fact that the following reaction,



is spin-forbidden, and its three-body reaction rate coefficient is many orders of magnitude slower than the formation channel for O_2 shown above. Therefore, the net result of the of CO_2 photolysis is



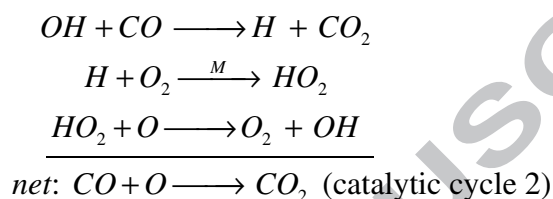
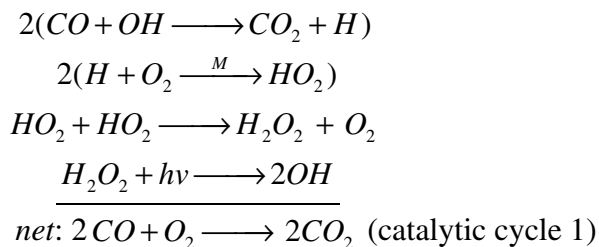
Within the context of a pure CO_2 atmosphere, the amounts of CO and O_2 would undoubtedly be very large, even when considering the photodissociation of O_2 :



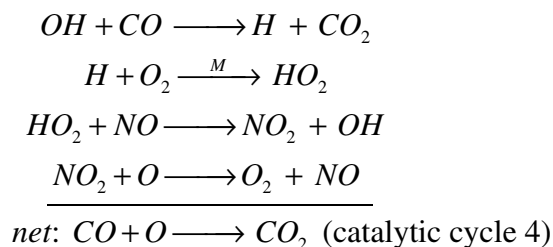
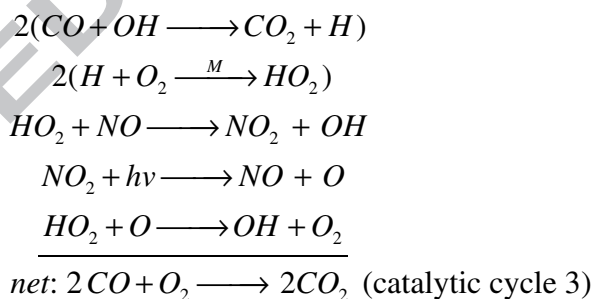
Specifically, this scenario yields CO and O_2 mixing ratios of 7.7×10^{-2} and 3.8×10^{-2} , respectively, and a CO: O_2 ratio of 2:1, which is in contradiction to the observed mixing ratios (7.0×10^{-4} for CO and 1.3×10^{-3} for O_2) and ratio of 0.5 (Yung and Demore, 1999). This suggests that another process stabilizes the observed CO_2 concentration of the Martian atmosphere.

The stability of CO_2 in the Martian atmosphere appeared to be a contradiction to known chemical kinetics for a pure CO_2 atmosphere, where for Mars, there was substantially smaller amounts of CO and O_2 – previously termed the CO_2 stability problem. It is well known that HO_x (H, OH, HO_2) chemistry plays an important role in stabilizing the CO_2 dominated atmosphere of Mars (McElroy and Donahue, 1972; Parkinson and Hunten, 1972). According to chemical mechanisms proposed by McElroy and Donahue (1972) (catalytic cycle 1) and Parkinson and

Hunte (1972) (catalytic cycle 2), CO is then effectively converted back to CO₂ via reactions with HO_x.



McElroy and Donahue (1972) and Parkinson and Hunten (1972) recognized that the small amount of water vapor in Mars's atmosphere could play a fundamental role in atmospheric photochemical processes. Since these seminal investigations, the only significant addition involved the reaction of HO₂ with NO to yield NO₂ and OH, which introduced 2 new chemical schemes for the oxidation of CO to CO₂ (Nair et al., 1994; Yung and Demore, 1999).



Since Nair et al. (1994), there has not been any significant update on addressing the CO-CO₂ cycling on Mars. The O(¹D) quantum yield has recently been updated, which quantifies nonzero quantum yields in the Huggins bands (Matsumi et al., 2002). In addition, it is also known that the

OH + CO reaction produces HOCO, a radical species, whose impact has never been considered in the Martian atmosphere, given the once limited kinetic data on reactions involving HOCO (Petty et al., 1993; Olkhov et al., 2001; Mielke et al., 2003; Yu et al., 2005). We, therefore, utilize the Caltech/JPL 1-D photochemical model for Mars to look at the impact on the chemical state of its atmosphere via the inclusion of updated O(¹D) quantum yields (Matsumi et al., 2002) and HOCO chemistry (Fulle et al., 1996; Sears et al., 1992) (**Table 1**). Firstly, the photochemical model setup is briefly described; thereafter, the impact on NO_y, HO_x, and CO_x chemistry are discussed in the Results and Discussion section.

II. Photochemical Model Setup

We utilize the Caltech/JPL one-dimensional (1-D) photochemical kinetics model for a latitude of 30° versus season, which is similar to that used by Yung et al. (1988) and Nair et al. (1994) to study the, overall, photochemical state of the Martian atmosphere. A detailed description of the 1-D photochemical model can be found in Nair et al. (1994); we, therefore, only provide a short description of the model. Specifically, it incorporates Mars atmospheric O_x, CO_x, HO_x, and NO_y chemistry in the presence of vertical diffusive transport and allows for time-dependent calculations. This model is an update of the Nair et al. (1994) model. It solves the 1-D continuity equation,

$$\frac{\partial n_i}{\partial t} + \frac{\partial \Phi_i}{\partial z} = P_i - L_i,$$

(n_i , Φ_i , P_i , and L_i are the concentration, vertical diffusive flux, and chemical production and loss terms, respectively, for species i (Allen et al., 1981) for 29 species (O, O(¹D), O₂, O₃, N, N(²D), N₂, N₂O, NO, NO₂, NO₃, N₂O₅, HNO₂, HNO₃, HO₂NO₂, H, H₂, H₂O, OH, HO₂, H₂O₂, CO, CO₂, O⁺, O₂⁺, CO₂⁺, and CO₂H⁺) in 177 reactions from the surface to the exosphere at 240 km (with 2 km resolution) in 121 levels. In the diurnally-averaged 1-D photochemical model, the steady-state solution is solved after allowing $\frac{\partial n_i}{\partial t} \longrightarrow 0$. The vertical flux is given by

$$\Phi_i = -D_i \left(\frac{dn_i}{dz} + \frac{n_i}{H_i} + \frac{n_i(1+\alpha)}{T} \frac{dT}{dz} \right) - K \left(\frac{dn_i}{dz} + \frac{n_i}{H_i} + \frac{n_i}{T} \frac{dT}{dz} \right),$$

where D_i is the molecular diffusion coefficient of species i through the background atmosphere, H_i is the scale height of species i , T is the temperature, α is the thermal diffusion factor (which we take to be zero), K is the eddy diffusion coefficient, and H is the scale height of the background atmosphere.

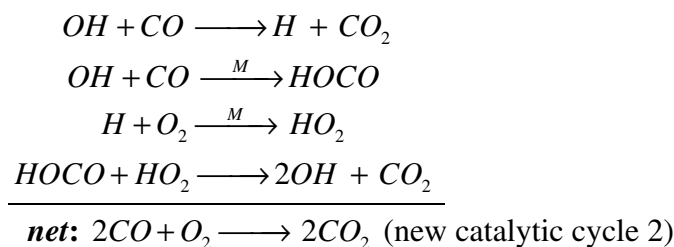
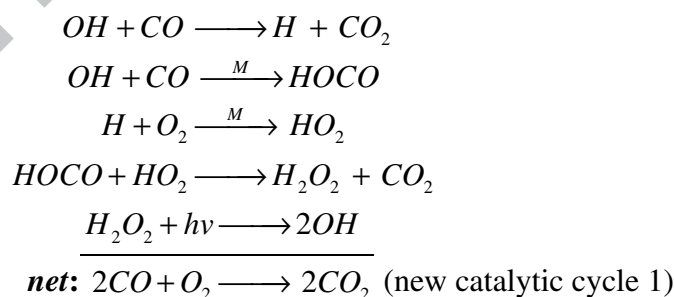
III. Results and Discussion

The HOCO chemistry completely represents all reactions sourced from the termolecular reaction pathway that produces HOCO (Petty et al., 1993; Olkhov et al., 2001; Clements et al., 2002; Yu et al., 2005; Sander et al., 2006; Lu et al., 2007; Yu et al., 2008a,b), while the updated representation of the production of $O(^1D)$ quantitatively includes the contributions of the photodissociation of vibrationally-excited ozone and the spin-forbidden dissociation channel (Matsumi et al., 2002). HO_x chemistry plays a vital role in stabilizing CO_2 in the Martian atmosphere. **Figure 1** displays a schematic of the principal pathways of the hydrogen species in the Martian atmosphere with the inclusion of HOCO chemistry.

The lifetime of HOCO in Earth's and Mars' atmosphere is defined by:

$$\tau_{(HOCO, Earth \text{ or } Mars)} = \left(\frac{1}{k_2[O_2]} \right).$$

Given Mars's small atmospheric O_2 content, pressure and temperature conditions, HOCO can be stabilized. Consequently, the lifetime of HOCO is much longer in its atmosphere (**Figure 2**), ranging from 90 ns and 30 μs at the Earth's and Mars's surface, respectively, to 1.2 days for Mars at 240 km. Using the HOCO reaction mechanism (**Table 1**), we propose two new reaction channels for converting CO to CO_2 on Mars that result from the new HOCO chemistry. Two catalytic cycles are shown below.



As shown in previously proposed catalytic cycles (McElroy and Donahue, 1972; Parkinson and Hunten, 1972; Yung and Demore, 1999) to convert CO to CO₂ on Mars, HO_x radicals are used as catalysts in the recombination of CO and O₂. Since HO_x radicals are not consumed in the chemical scheme, very few molecules are needed. Under Martian atmospheric conditions, the production of HOCO will be governed by its low-pressure limiting rate constant (Sander et al., 2006). **Figure 3 (a)** displays a 1-D simulation of the mixing ratio of HOCO as a function of altitude. Although the loss of HOCO is dominated by its reaction with O₂, its mixing ratio profile is governed predominantly by the concentration of OH (**Figure 3 (b)**) as it is solely produced by the reaction of OH+CO+M, where 'M' (or the third body) on Mars is CO₂. Using the rate constants from Sander et al. (2006) for the reaction of OH+CO to produce H+CO₂ and HOCO, does not affect the column abundance of CO. Even though the current understanding of Martian atmospheric chemistry does not fully account for CO measured from spacecraft (Rosenqvist et al., 1992; Encrenaz et al., 2006) and earth-based (Clancy et al., 1990; Lellouch et al., 1989; Krasnopolsky, 2003; Krasnopolsky, 2007) observations, our simulation of CO (200 ppmv) are in accord with recent and past measurements of CO in the Martian atmosphere, which range from 200 to 1250 ppmv (Smith et al., 2001).

The primary impact of the HOCO chemistry is that it contributes, via the reaction of HCO₂ and O₂, up to 5% (at 22 km) towards the production of CO₂. Frost et al. (1993) and Senosiain et al. (2003) represent the only experimental and theoretical study that has quantified rate constants for the OH+CO reaction under Martian conditions. Yet, recent experimental and theoretically-obtained branching ratios (*i.e.*, for HOCO and H+CO₂ via OH+CO), by Clements et al. (2002) and Lu et al. (2007) imply a factor of 8 to 60 increase in the HOCO total column abundance. In addition, these sensitivity simulations also reveal that HOCO may contribute 25 to 70% towards the production of CO₂ from the surface up to 44 and 50 km (**see supplementary material**). These sensitivity simulations do not affect the concentrations of CO and CO₂, but imply that the conversion of CO to CO₂ may proceed largely through the HOCO chemical mechanism. Still, based on the current understanding of atmospheric chemistry, balancing CO₂ production and loss, has still proven to be difficult to accurately resolve (Atreya, 1990; Atreya, 1994; Krasnopolsky, 2006). These simulations also show perturbations to column abundances of NO_y and HO_x, ranging from 15% to a factor of 3 (**Figure 4a-m**).

The inclusion of an updated representation of the $O(^1D)$ quantum yield effects NO_y , CO_x , and HO_x species, ranging from ~ 5 to 50% with respect to their column abundances (**Figure 4a-m and Figure 5a-b**). HO_2NO_2 exhibits the largest perturbation to its total column abundance (45% increase) of all NO_y species, which is due to increases in NO , NO_2 , NO_3 , N_2O_5 , HO_2 , HNO_3 and HNO_2 , ranging from ~ 10 to 40%. The most drastic increase in HO_x is due to a 20% increase in HO_2 , due to inclusion of the new HOCO reaction channel, $HOCO+O_2$. H_2 exhibits a 25% reduction in its column abundance. This is due to the fact that there is a reduction in the rate of H_2 formation from its primary production channel ($H+HO_2 \rightarrow H_2+O_2$). OH and H_2O_2 exhibit 10% decrease and 50% increase, respectively, in their total column abundance (note: perturbations are mostly pronounced in Mars' lower atmosphere as exemplified in **Figure 6a-b**). The decrease in OH is due to the production of HOCO via $OH+CO+M$, and the increase in H_2O_2 is a result of increasing contribution from the HO_2 self-reactions ($2HO_2 \rightarrow H_2O_2+O_2$ and $2HO_2 \rightarrow H_2O_2+O_2(^1\Delta)$). Recent earth- and satellite-based measurements of H_2O_2 (15 ppbv) (Smith et al., 2009) show that our simulations with the inclusion of the updated $O(^1D)$ quantum yields and HOCO reaction cycles are in comparable agreement with H_2O_2 (5 ppbv).

IV. Conclusions

Given the substantially longer lifetime of HOCO in Mars's atmosphere, compared to Earth, we examine the inclusion of novel HOCO chemical cycles in a 1-D photochemical model for Mars in addition to the most recent representation of the $O(^1D)$ quantum yield. Our simulations, constrained by laboratory and theoretical (*i.e.*, first principle *ab initio*) rate data (Sander et al., 2006; Petty and Moore, 1993; Nair et al., 1994; Yu and Francisco, 2008) involving HOCO and an updated representation of the $O(^1D)$ quantum yield (Matsumi et al., 2002), show significant effects on Mars' atmospheric NO_y , HO_x , and CO_x chemistry and also its oxidative capacity. Similar to HO_x radicals, the HOCO chemical cycles show that H_2O_2 is more intimately linked to CO_x chemistry through the production of HOCO. The present work demonstrates that HOCO is a significant new member of the HO_x family, not previously accounted for in earlier studies of chemistry on Mars. This analysis also provides important new detection limits for target trace gas species for the ExoMars Trace Gas Orbiter Mission, scheduled for launch in 2016. Lastly, given recent advancements elucidating the importance of quantum tunneling in the $OH+CO$ reaction (regarding the loss of H from excited states of HOCO) should be further investigated via atmospheric modeling as its impact via HOCO-related chemical cycles may prove impactful

(Johnson et al., 2010; Johnson et al., 2011; Nguyen et al., 2012; Wang and Bowman, 2014; Wang et al., 2014).

ACCEPTED MANUSCRIPT

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Captions

Figure 1. Schematic diagram showing the principal pathways for reactions involving hydrogen species. The red and green arrows illustrate new reactions included in the Caltech/JPL 1-D photochemical sourced from O_3 photolysis and the $OH+CO$ reaction, which affect odd hydrogen chemistry.

Figure 2. HOCO lifetime (min.) vs altitude (km) for and Mars.

Figure 3. (a) Altitude (km) versus HOCO mixing ratio. (b) Altitude (km) versus OH concentration.

Figure 4. (a through m) Altitude (km) versus mixing ratio plots for NO_y and HO_x species. Note: the $OH+CO$ branching ratio simulation plot represents species via simulations incorporating the recent experimentally-obtained branching ratios for the oxidation of CO (Clements et al., 2002; Lu et al., 2007).

Figure 5. (a) Altitude (km) versus CO mixing ratio. (b) Altitude (km) versus CO_2 concentration.

Figure 6. (a) Altitude (km) versus $[OH]_{with-new-chemistry} - [OH]_{without-new-chemistry}$. (b) Altitude (km) versus $[H_2O_2]_{with-new-chemistry} - [H_2O_2]_{without-new-chemistry}$.

Table 1

New Reactions included in the JPL/Caltech 1-D Photochemical Mars Model. Rate coefficients are given in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for bimolecular and $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ for termolecular reactions.

	Reaction	Rate Coefficient	Reference
R_1	$\text{OH} + \text{CO} + \text{M} \rightarrow \text{M} + \text{HCO}_2$	$k_0 = 5.90\text{E-}33 (\text{T}/300)^{-1.4}$	Sander et al. (2006)
R_2	$\text{HCO}_2 + \text{O}_2 \rightarrow \text{HNO}_2 + \text{CO}_2$	2.00×10^{-12}	Sander et al. (2006)
R_3	$\text{HCO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{CO}_2$	5.80×10^{-11}	Yu et al. (2008)
R_4	$\text{HCO}_2 + \text{HO}_2 \rightarrow 2\text{O}_2 + \text{CO}_2$	6.50×10^{-12}	Yu et al. (2008)
R_5	$\text{HCO}_2 + \text{H} \rightarrow \text{H}_2 + \text{CO}_2$	1.00×10^{-10}	Yu and Francisco (2008)
R_6	$\text{HCO}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{CO}$	4.00×10^{-12}	Yu and Francisco (2008)
R_7	$\text{HCO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}_2$	1.00×10^{-11}	Yu et al. (2005)
R_8	$\text{HCO}_2 + \text{NO} \rightarrow \text{HNO}_2 + \text{CO}$	2.00×10^{-12}	Olkhov et al. (2001)

Figure 1

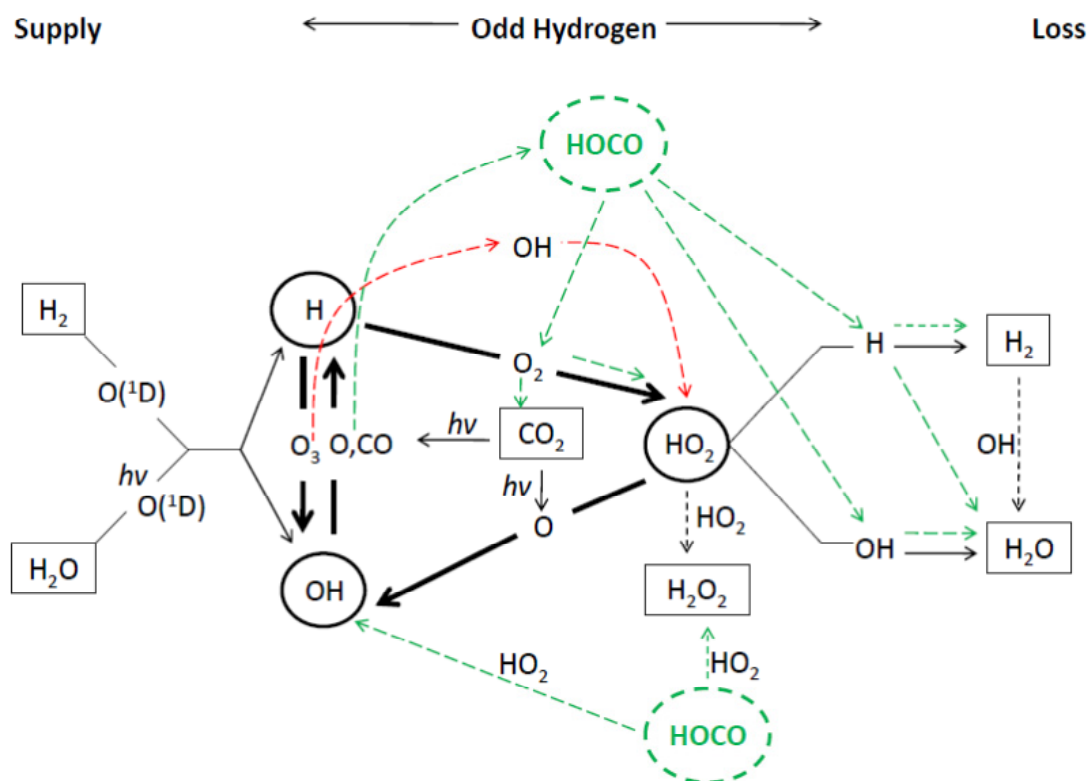


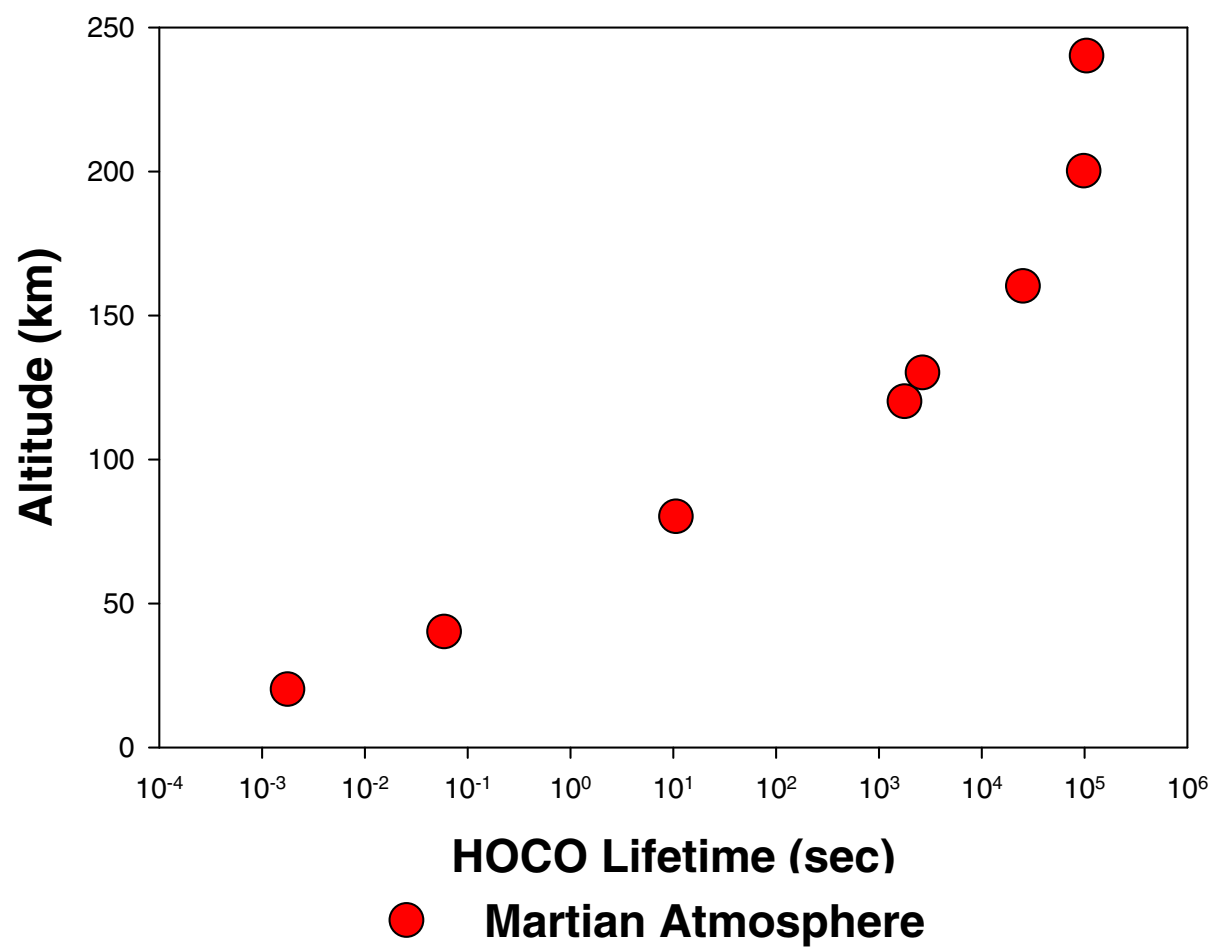
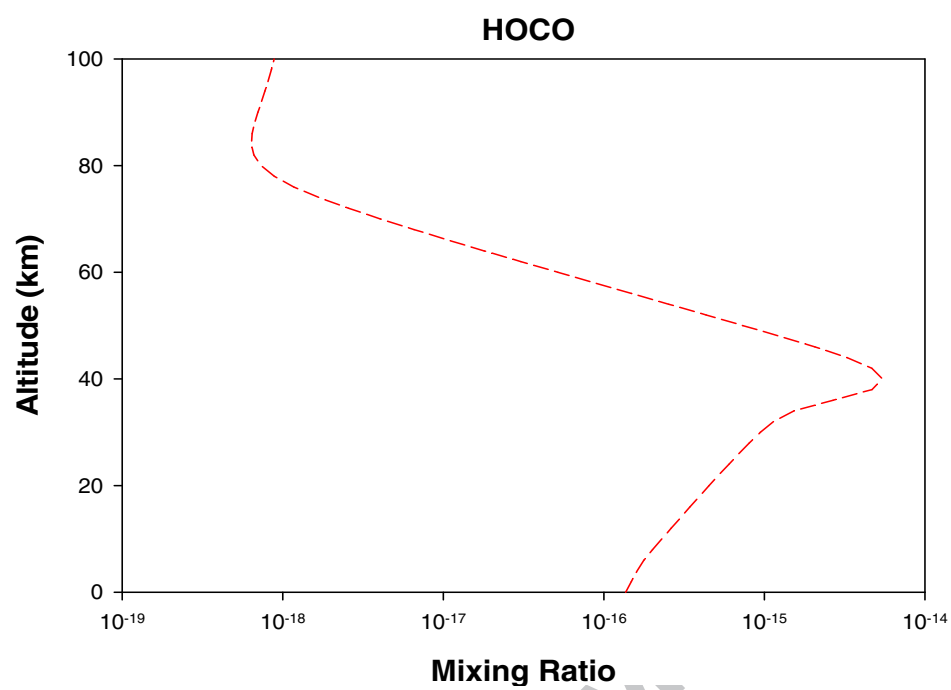
Figure 2

Figure 3

(a)



(b)

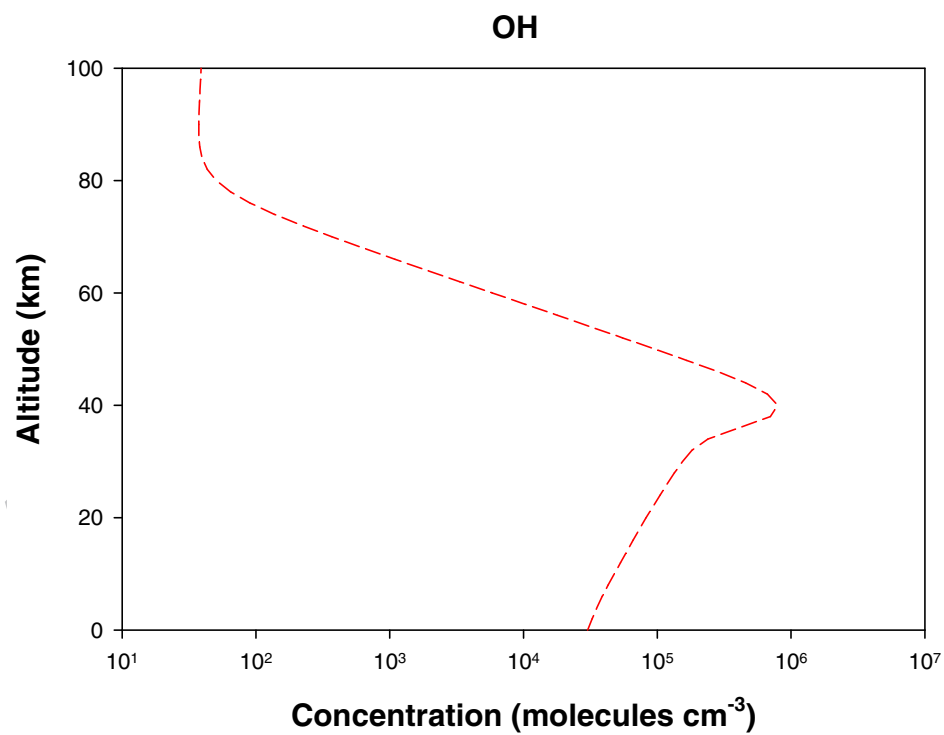
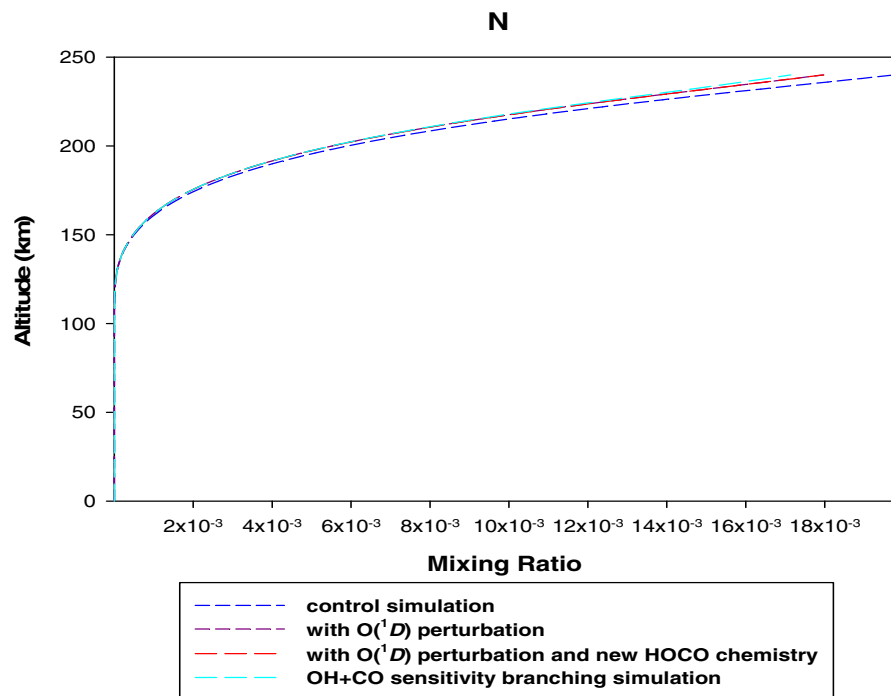
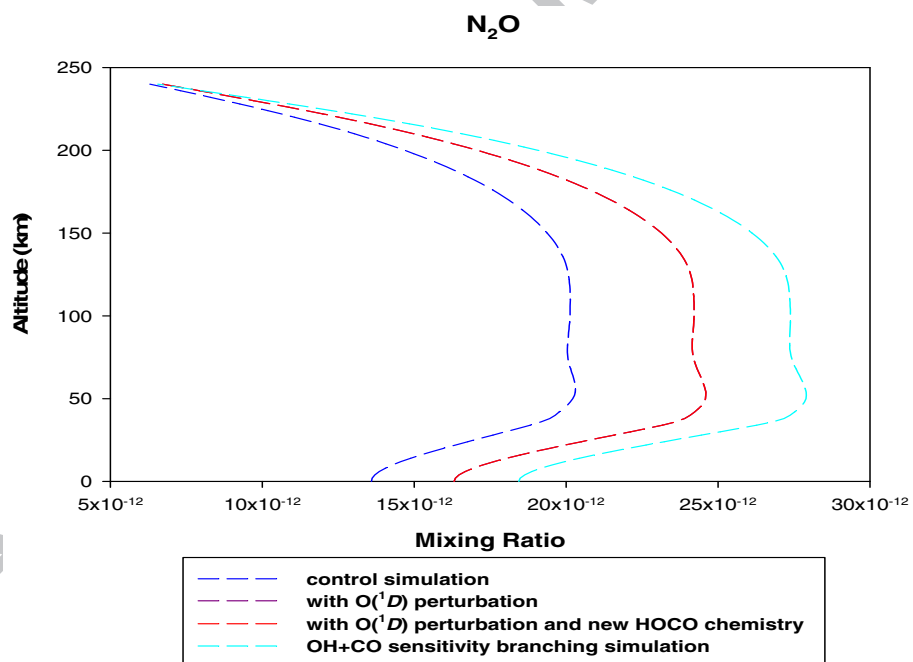


Figure 4

(a)

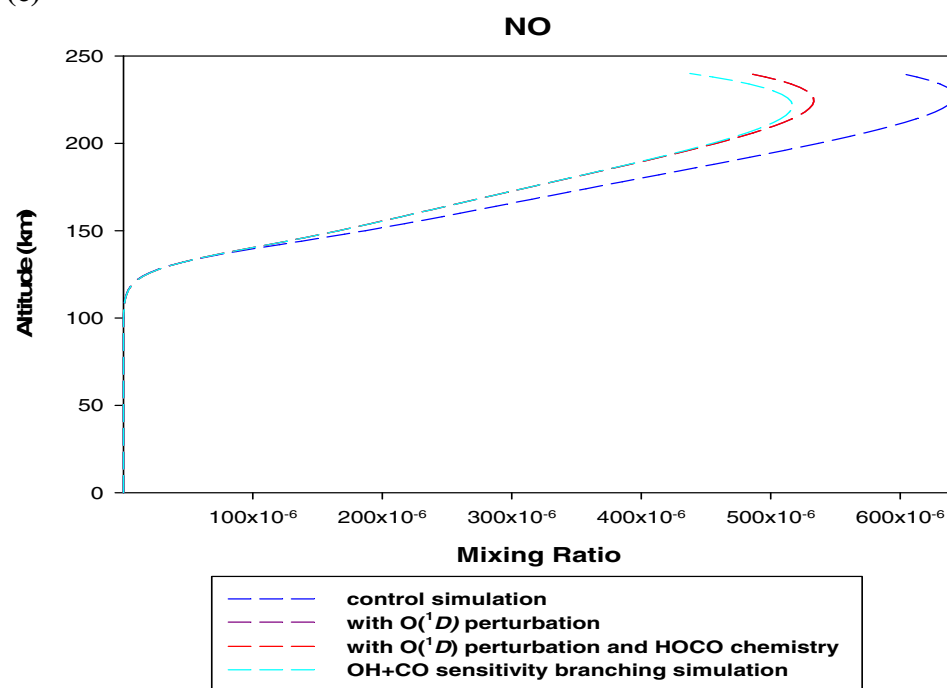


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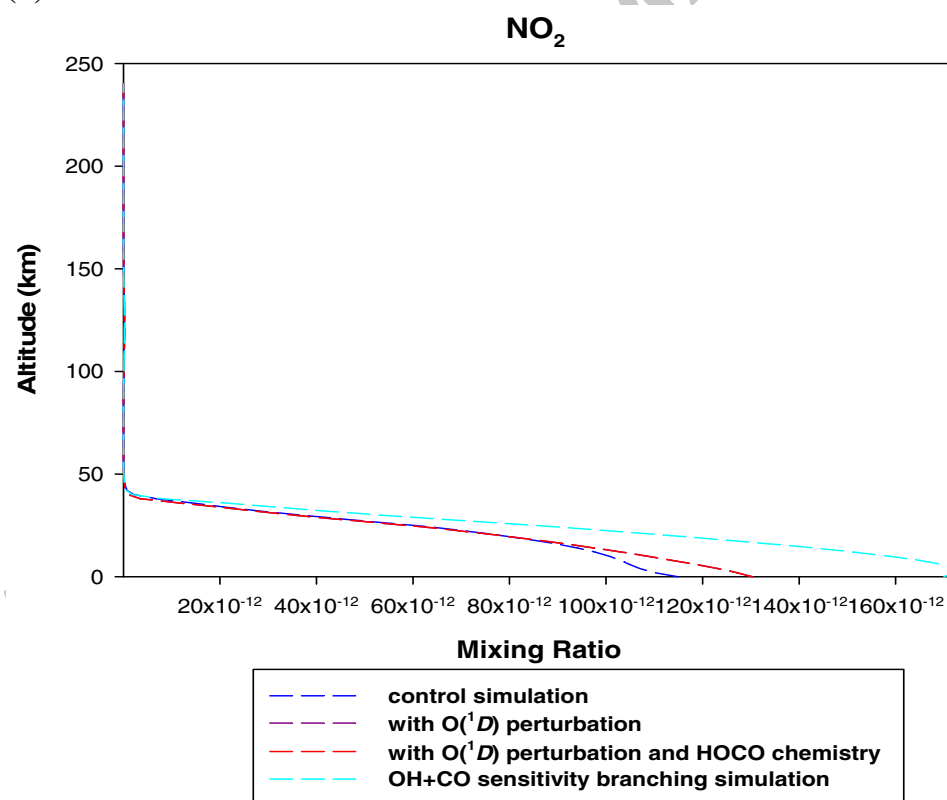


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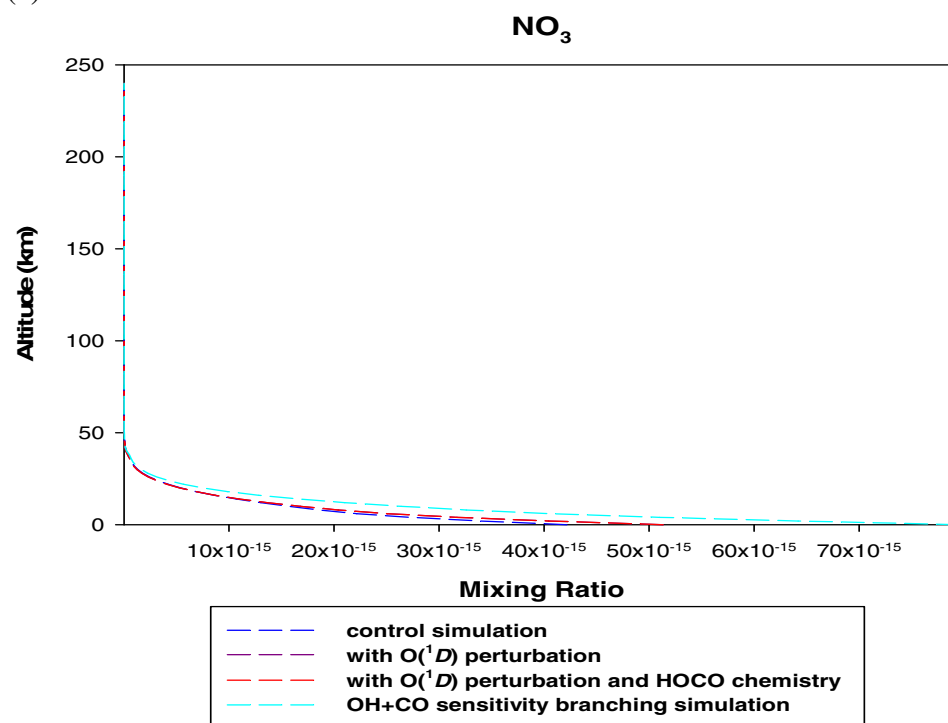
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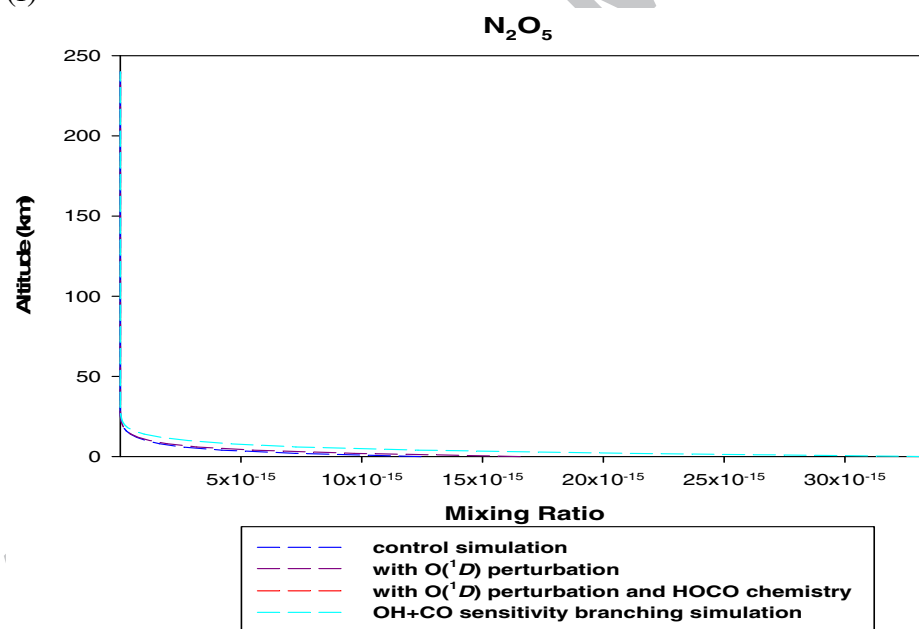
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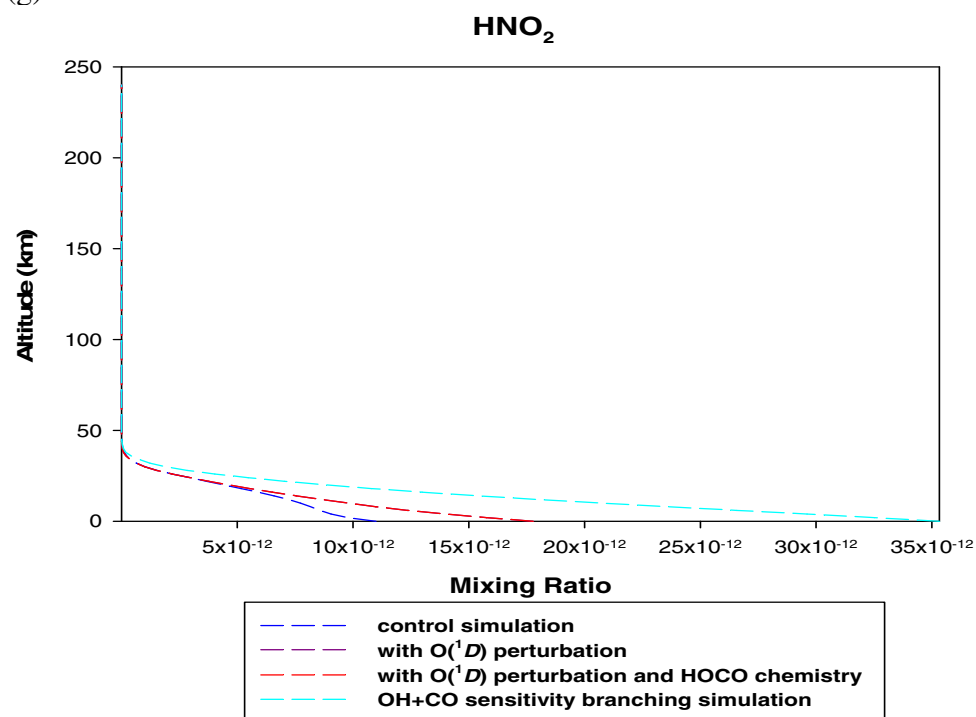
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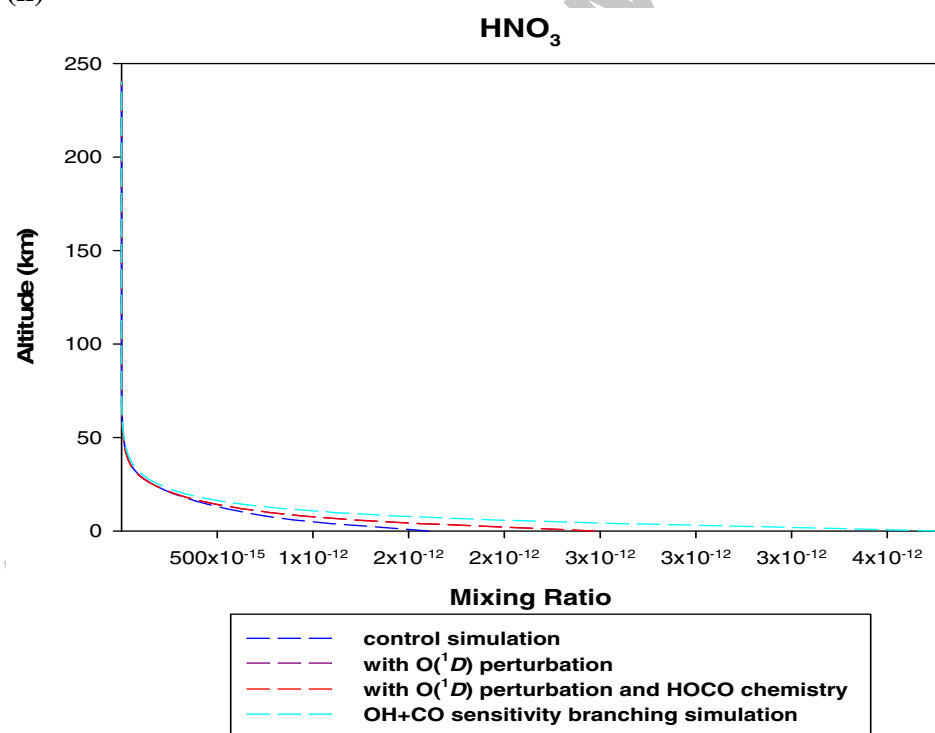
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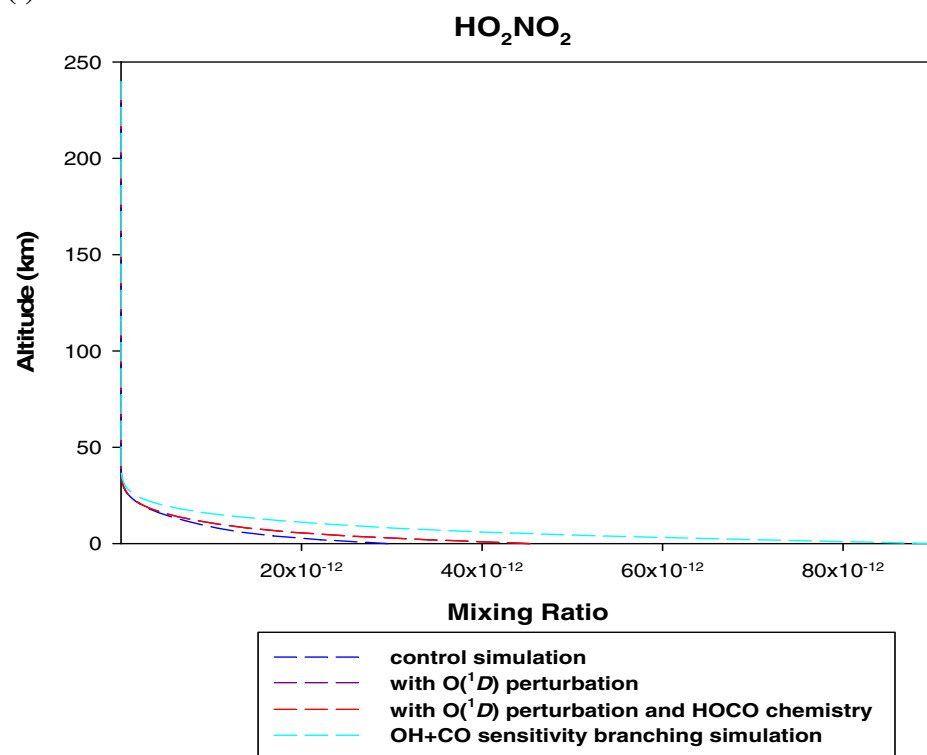
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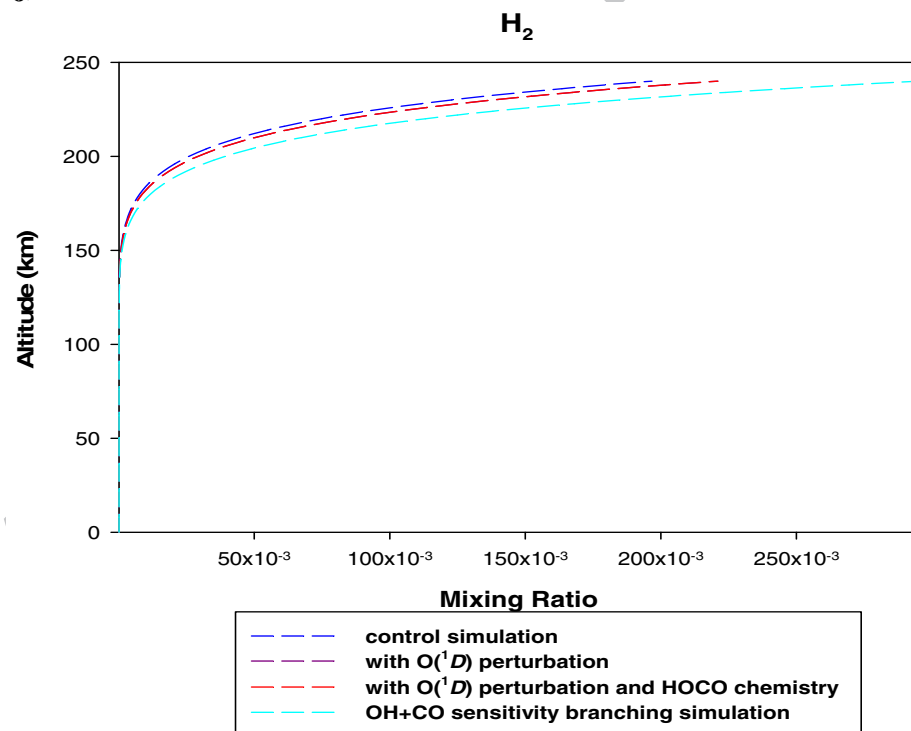
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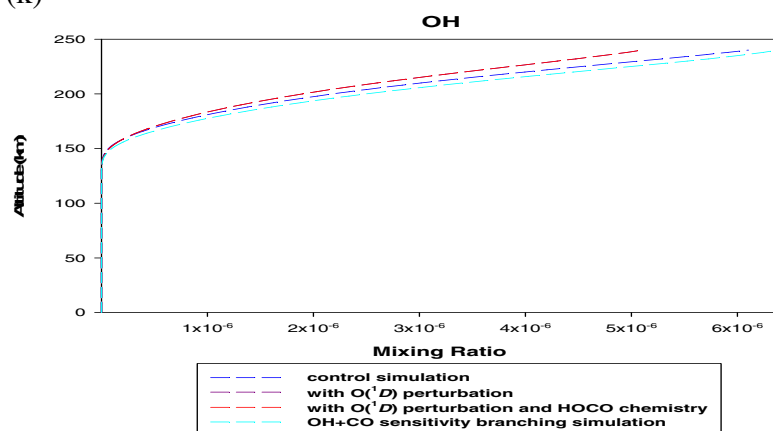
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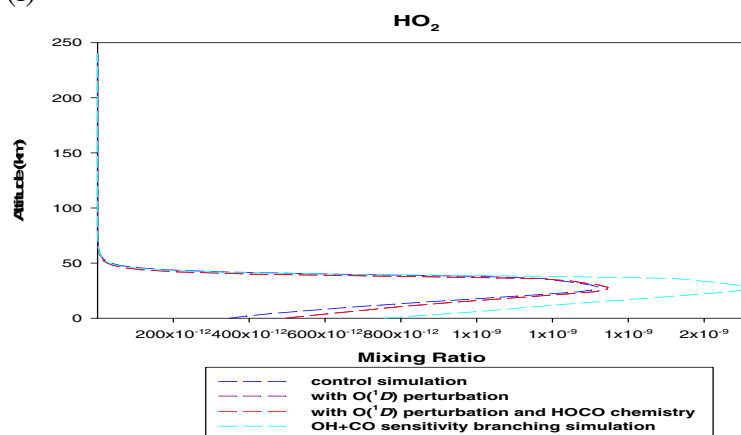
(j)



(k)



(l)



(m)

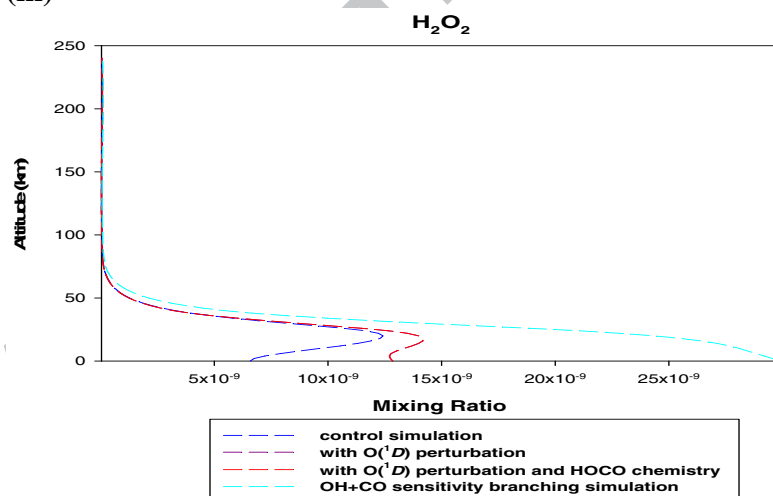
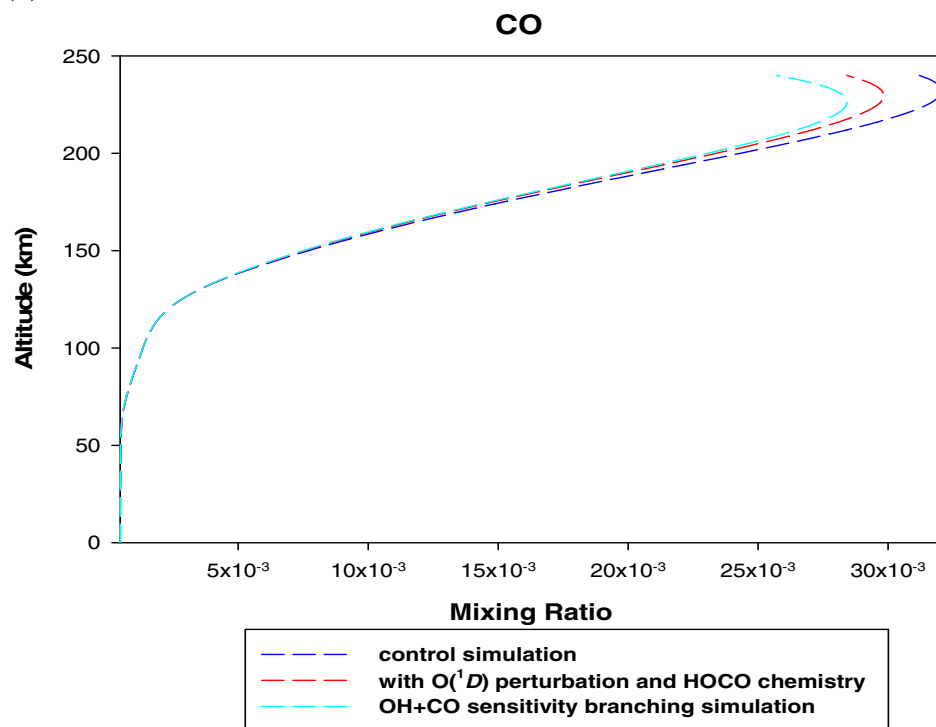


Figure 5

(a)



(b)

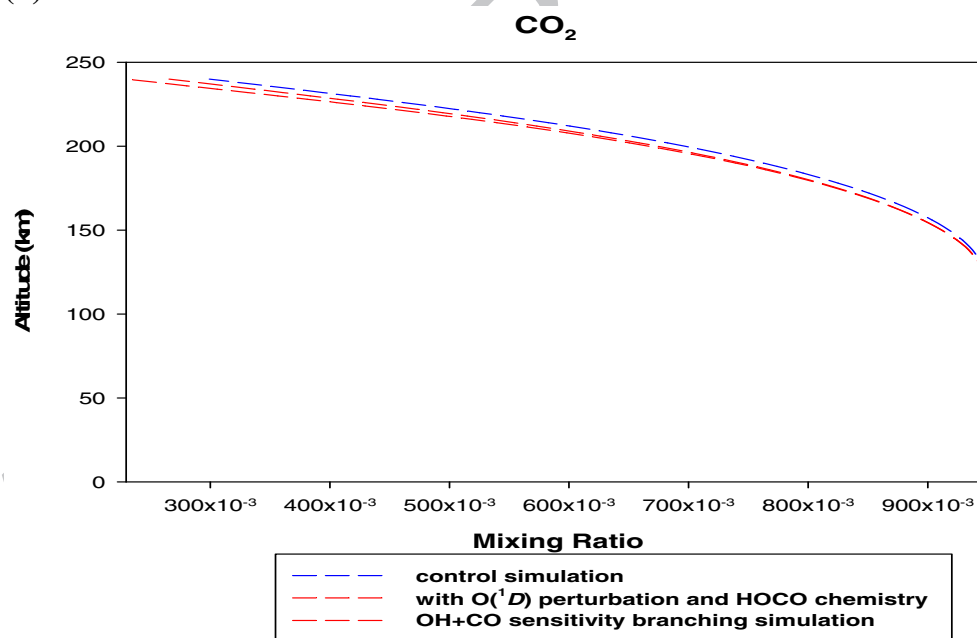
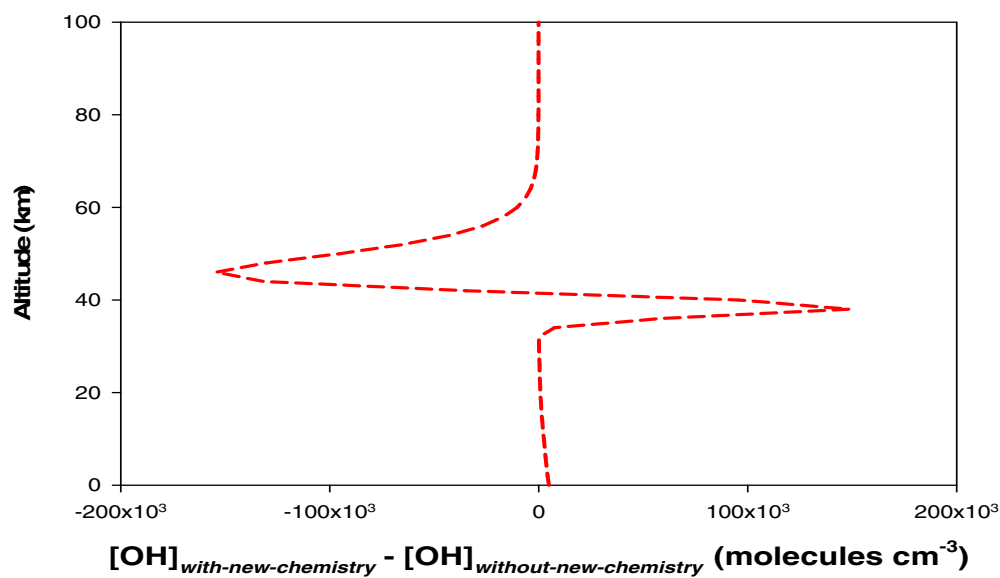


Figure 6

(a)



(b)

